Titanium Dioxide:
A brief overview of TiO2 Pigments compared with TiO2 Nanomaterials

March 2010

DUPONT®

The miracles of science™

TiO2 Pigment Compared with TiO2 Nanomaterials

Pigmentary TiO2 primary size is best if greater than 250 nm

- Excellent Light Scattering
- Optimized to scatter visible light – makes things appear white
- Absorbs UV light

Nano TiO2 primary particle size is 100 nm or less (by definition)

- Optimized to absorb UV light (sunscreens & protection)

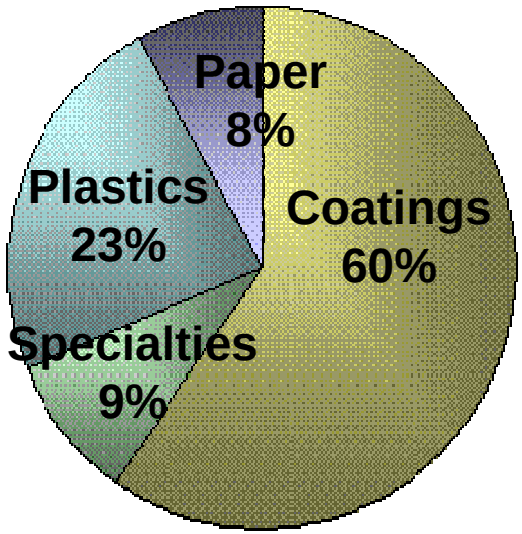
or

- Optimized for other desired end-use properties
  - High surface area (catalysis)
  - Selective wavelength scattering (color effects)

Pigmentary Titanium Dioxide

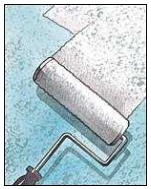
Premium white pigment

- $9 Billion global Market
- Highest “Hiding Power”
- Critical ingredient
- Coatings, Plastics, Paper and Paper Laminates
- Other applications
  - Printing inks, floor coverings, ceramics, textiles and fibers



TiO_2: Decorative & Protective

Coatings



Plastics



Paper

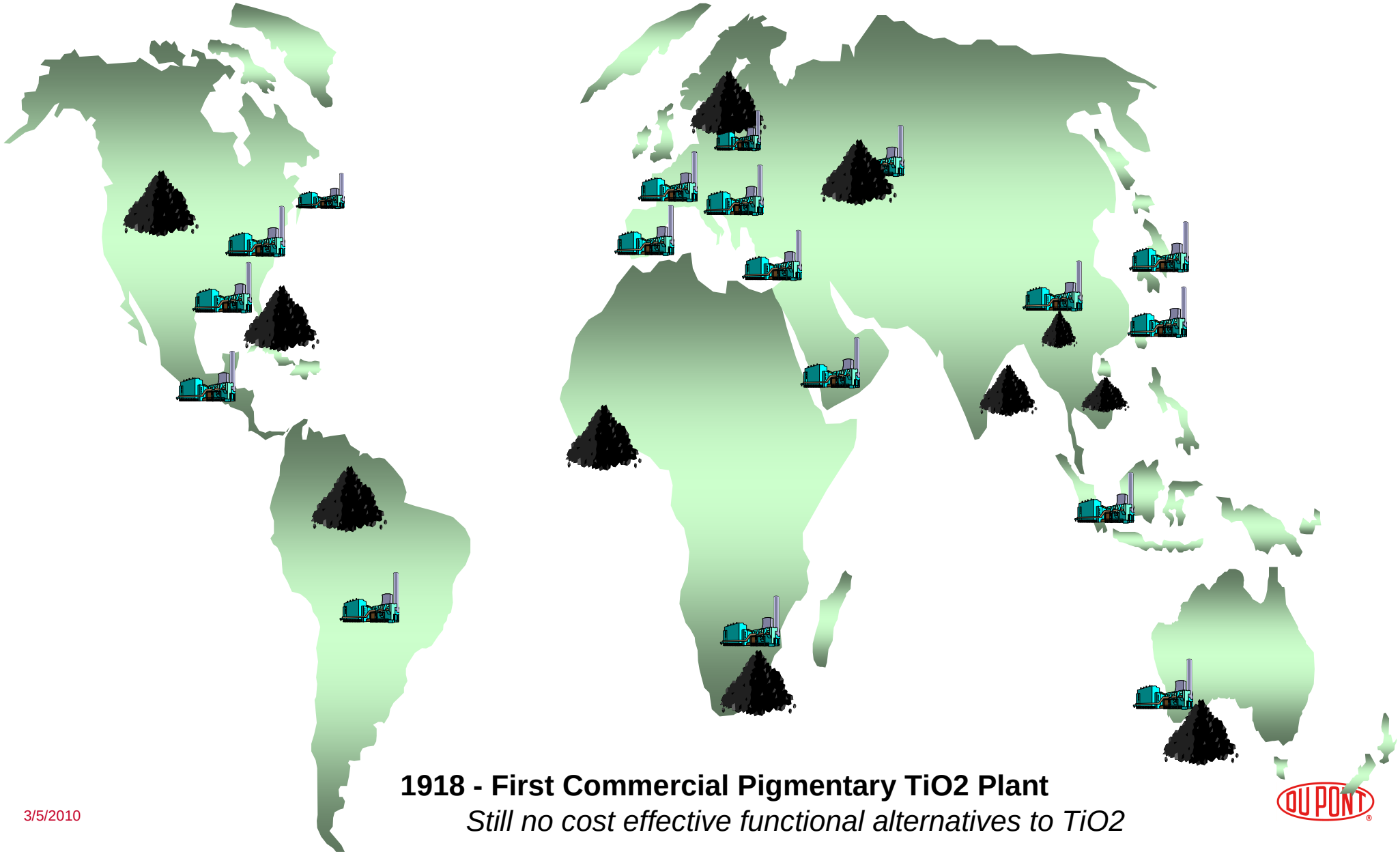
Specialties







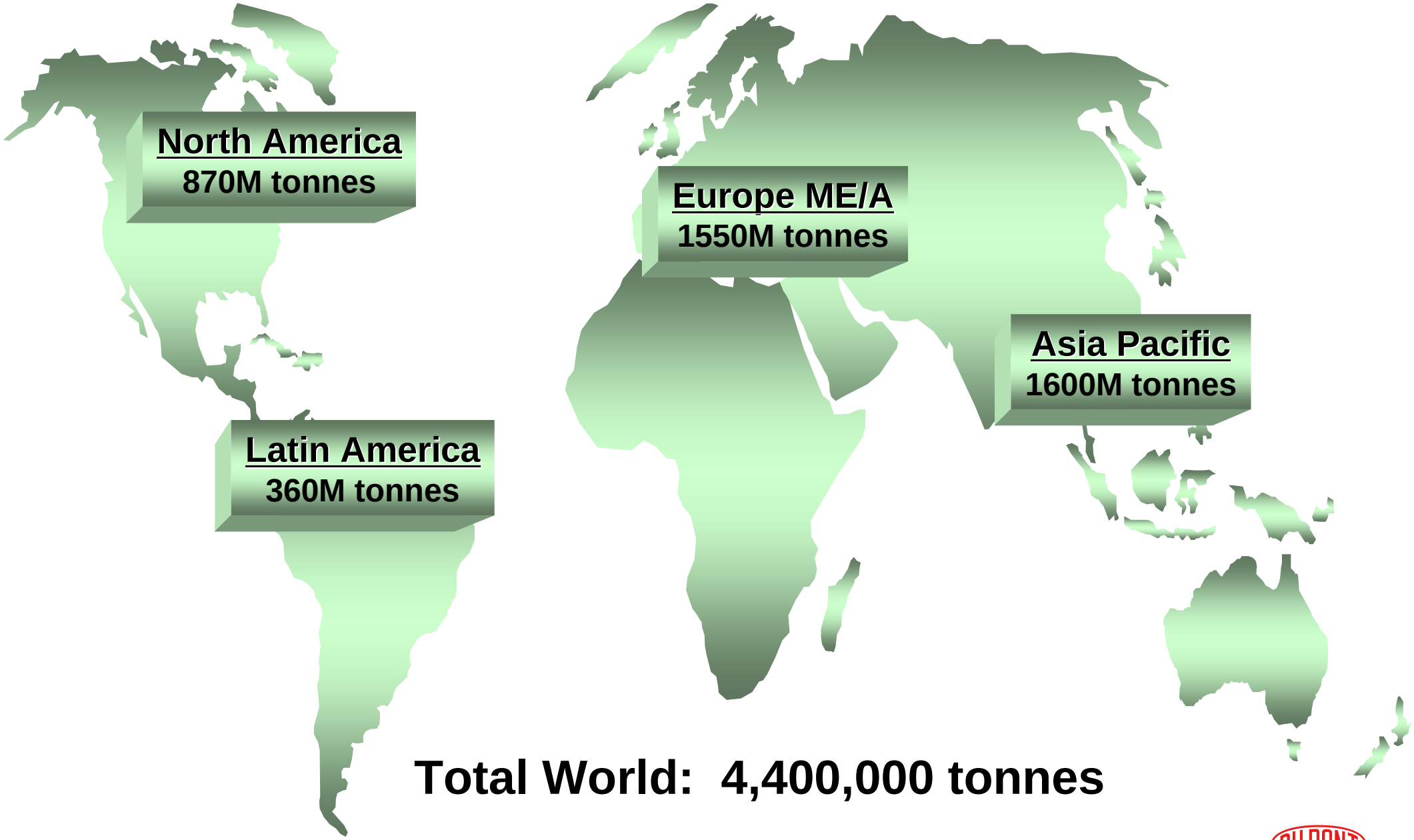
Pigmentary TiO2 - A Global Industry
TiO2 Pigment Plants & Ore Sources



1918 - First Commercial Pigmentary TiO2 Plant

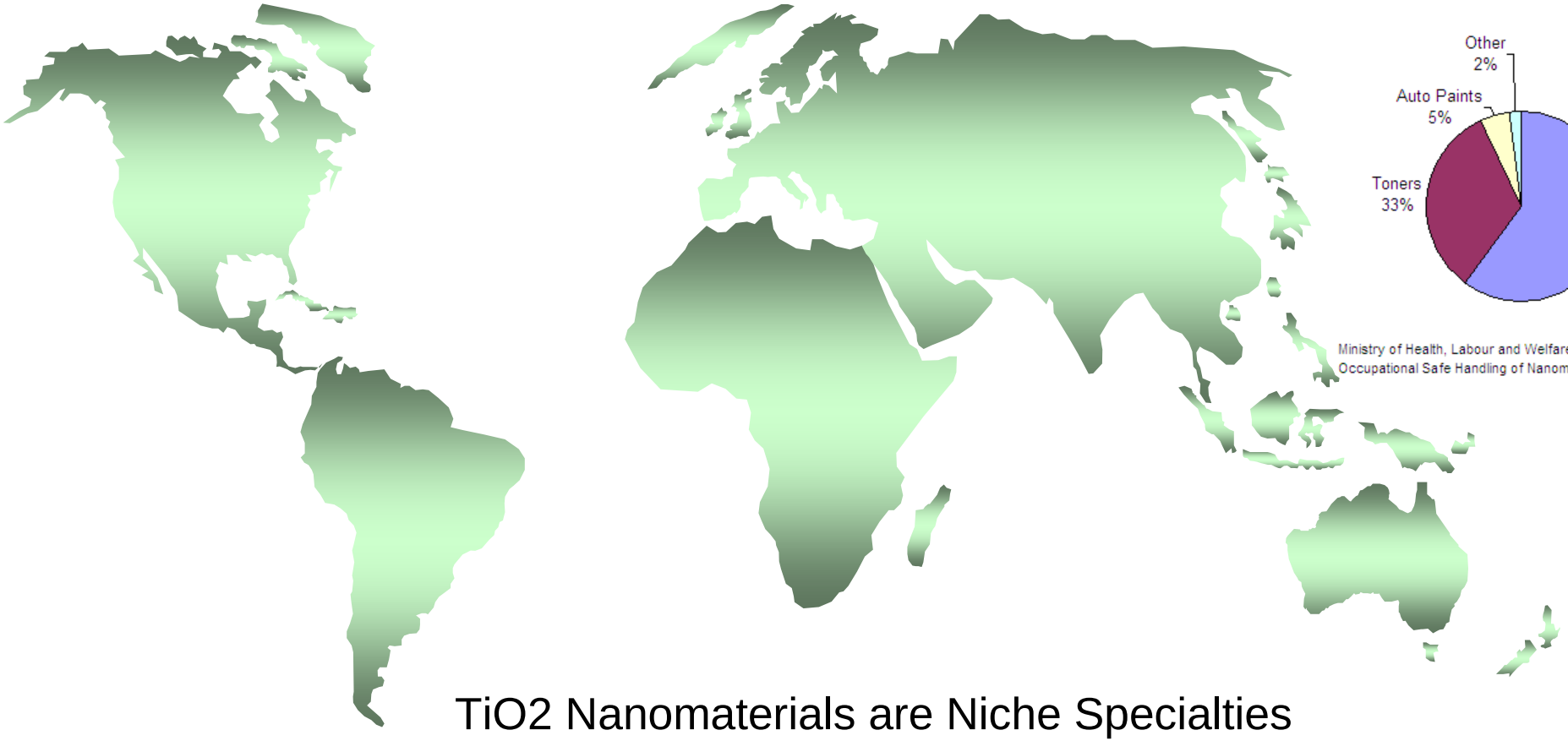
Still no cost effective functional alternatives to TiO2

World Pigmentary TiO_2 Market Demand (estimate)



Total World: 4,400,000 tonnes

Total World Nano TiO2 Demand: <0.6% of TiO2 Pigmentary Demand



Usage of TiO2 Nanomaterials (Japan)
(Japan Production ~2500 tonnes)

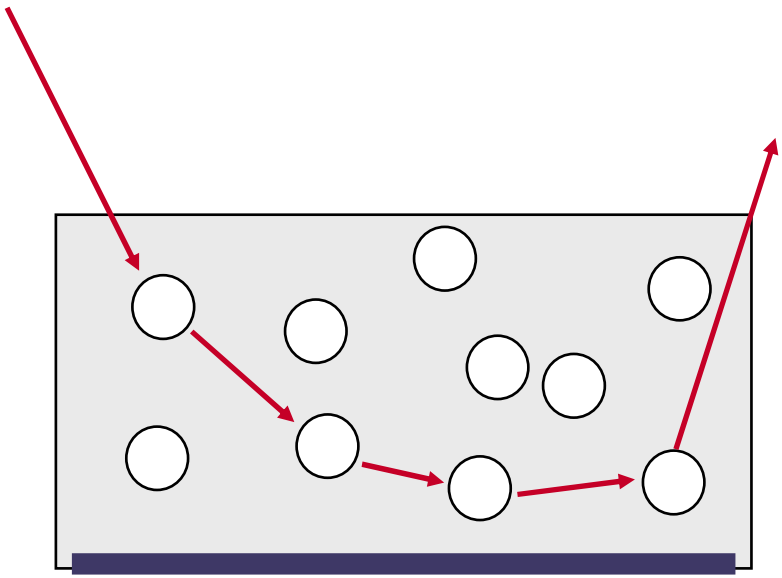
Ministry of Health, Labour and Welfare, "Study Group Report: Occupational Safe Handling of Nanomaterials", March 2009.

TiO2 Nanomaterials are Niche Specialties

Opacity influenced by Refractive Index

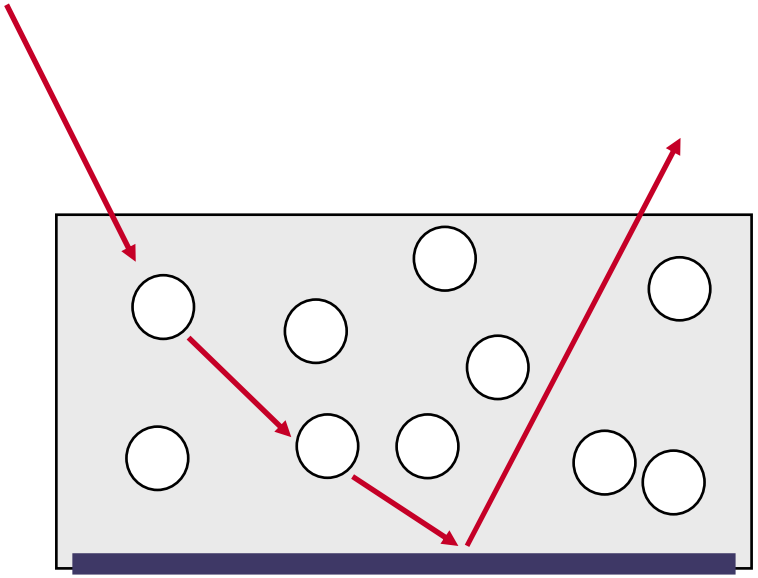
$$\text{Scattering} \sim (\eta_1 - \eta_2)^2$$

VIS



TiO2 has High R.I. –
High Scattering Efficiency

VIS



Low R.I. Materials –
Low Scattering Efficiency

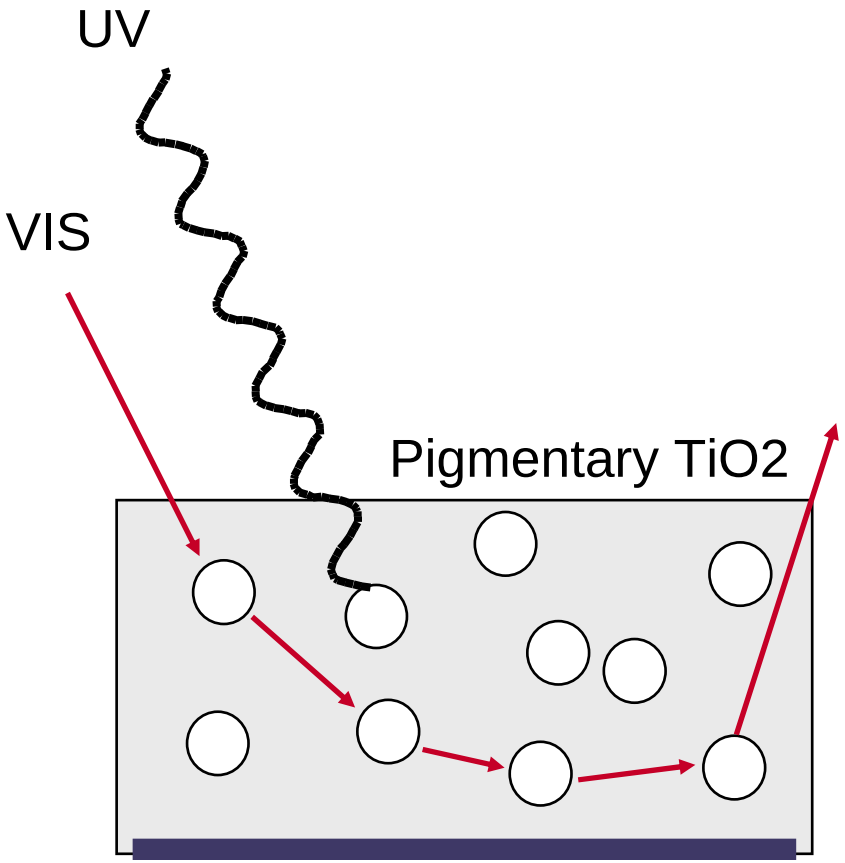
Scattering Efficiency vs. Refractive Index

CLAY	CALCIUM CARBONATE	ZINC OXIDE	ANATASE TiO_2	RUTILE TiO_2

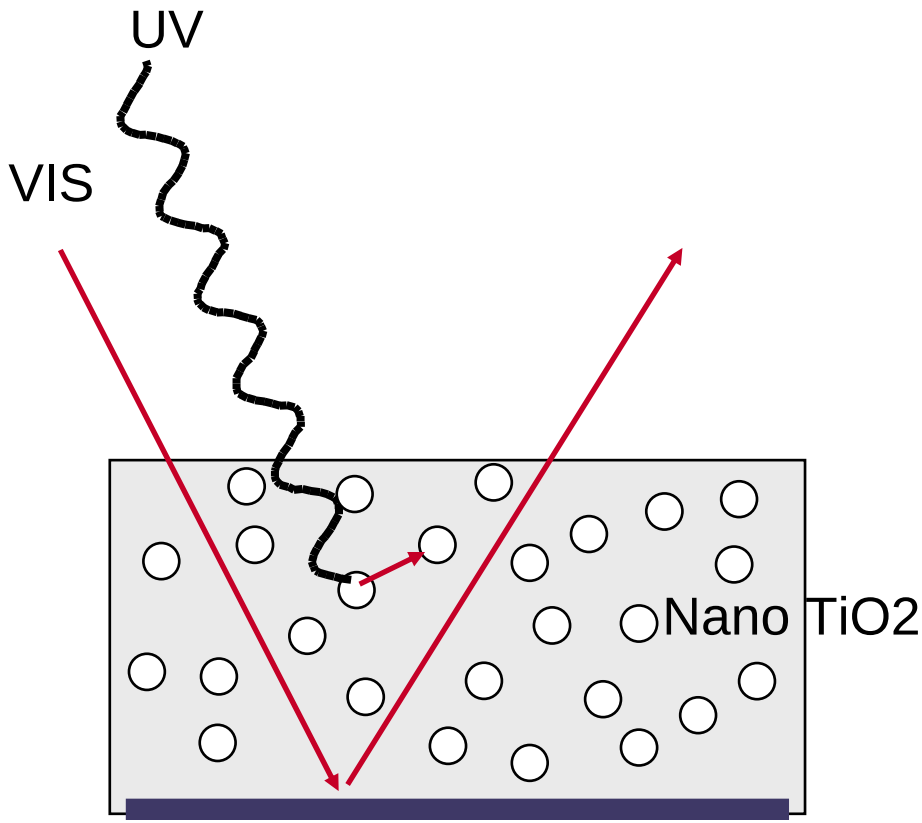
η	1.55	1.65	2.00	2.55	2.73

$$\text{Scattering} \sim (\eta_1 - \eta_2)^2$$

Opacity (Vis) & UV - Particle Size Matters



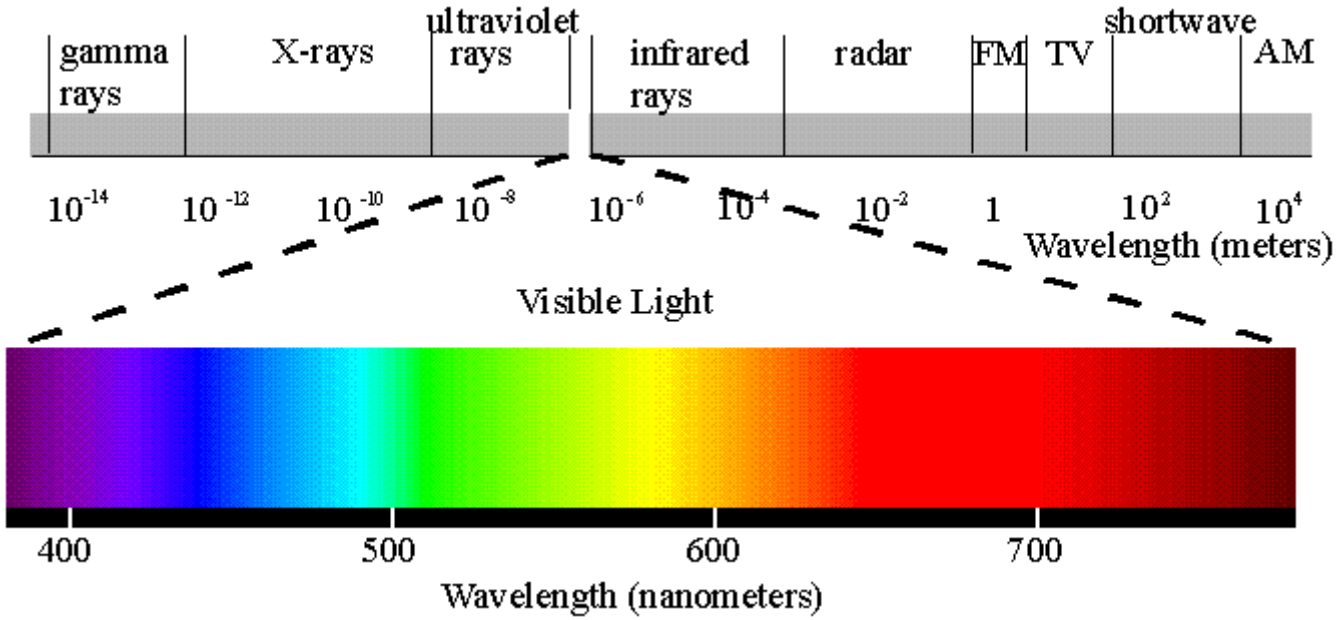
**TiO2 has high R.I. –
High Scattering Efficiency
Also absorbs UV**



**Smaller Size “nano” -
Low Visible Scattering
Efficiency**

TiO2 particles cannot be broken down even by extensive grinding

Optimal Scattering of Pigmentary TiO2



The optimal particle size is calculated from Weber's Law:

$$D = \frac{2\lambda}{\pi(n_1 - n_2)}$$

D = Particle Diameter
n = refractive index of (1) Particle and (2) Resin

2*550/(3.14*(2.7-1.5) ~ say 290 nm

Spectrum from www.dnr.sc.gov/.../pipb/lecture/lecture.html

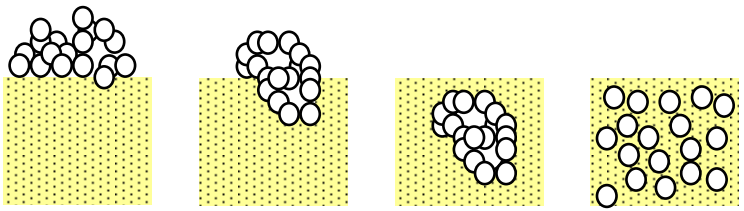
Influence of Surface Treatment

Bulk Properties of TiO_2:

- Light Scattering
- UV Absorbance

Surface Properties of TiO_2:

- Durability – Isolates the TiO2
- Gloss
- Opacity
- Ease-of-dispersion / dispersibility
- Compatibility with other components
- Viscosity



Surface Treatments

Material Requirements

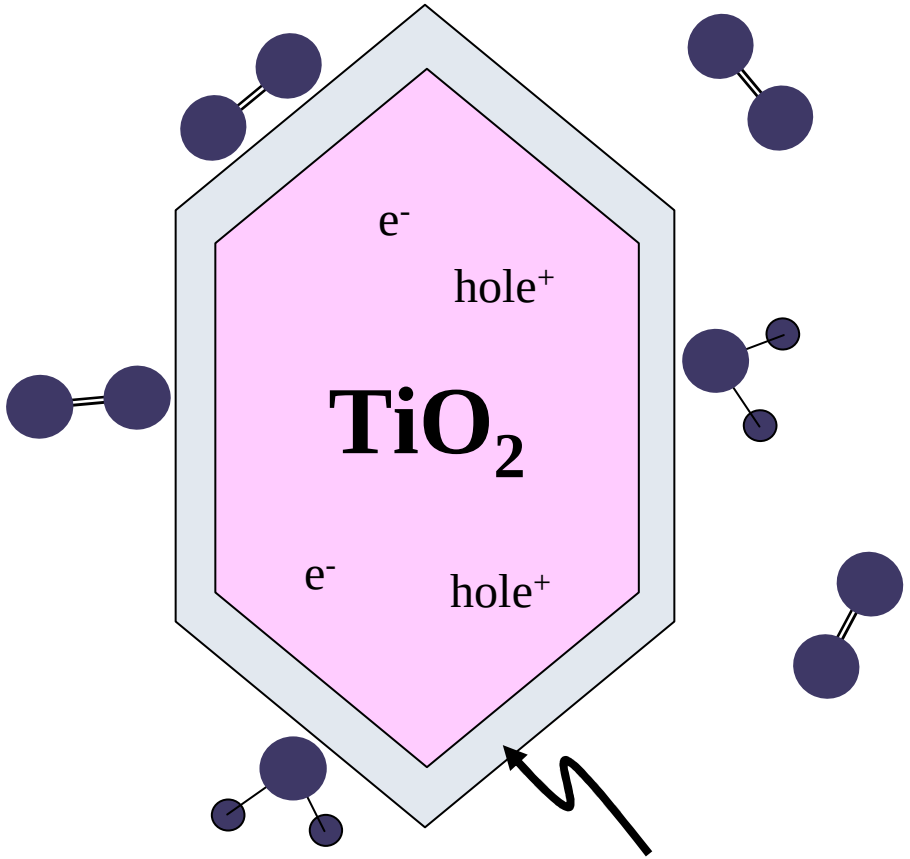
- Colorless
- Non-toxic
- Insoluble
- Inexpensive
- Easy to handle

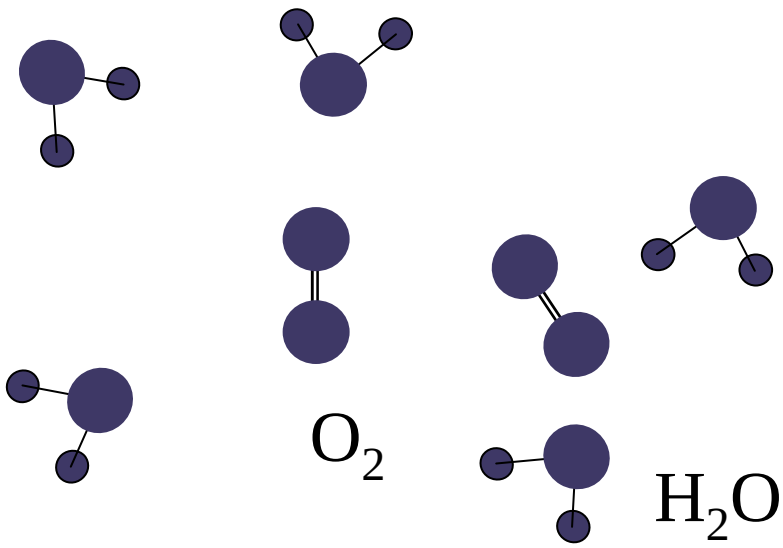
Compounds Used

- Hydrous alumina
- Hydrous silica
- Zirconia
- Select Organics

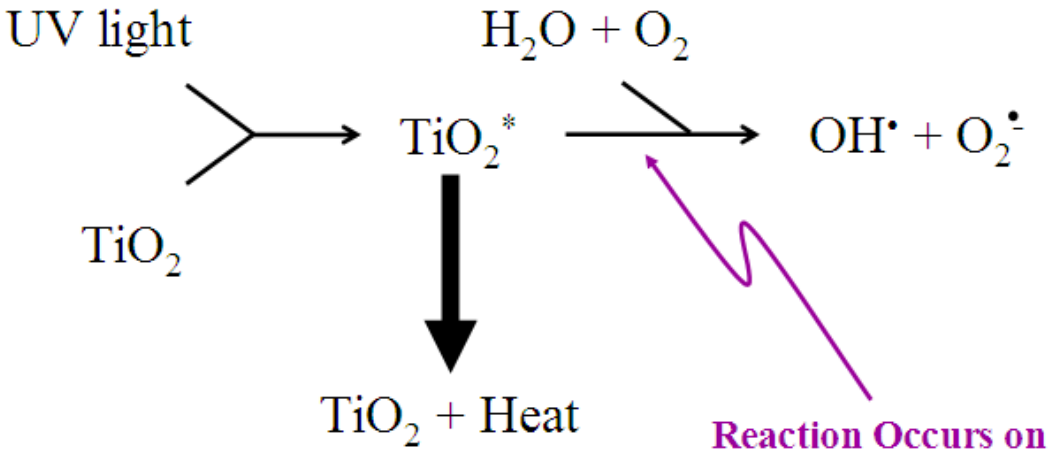
Surface Treatments Minimize Photocatalysis

Barrier Layer Protection





Barrier Layer



Dispelling Misinformation

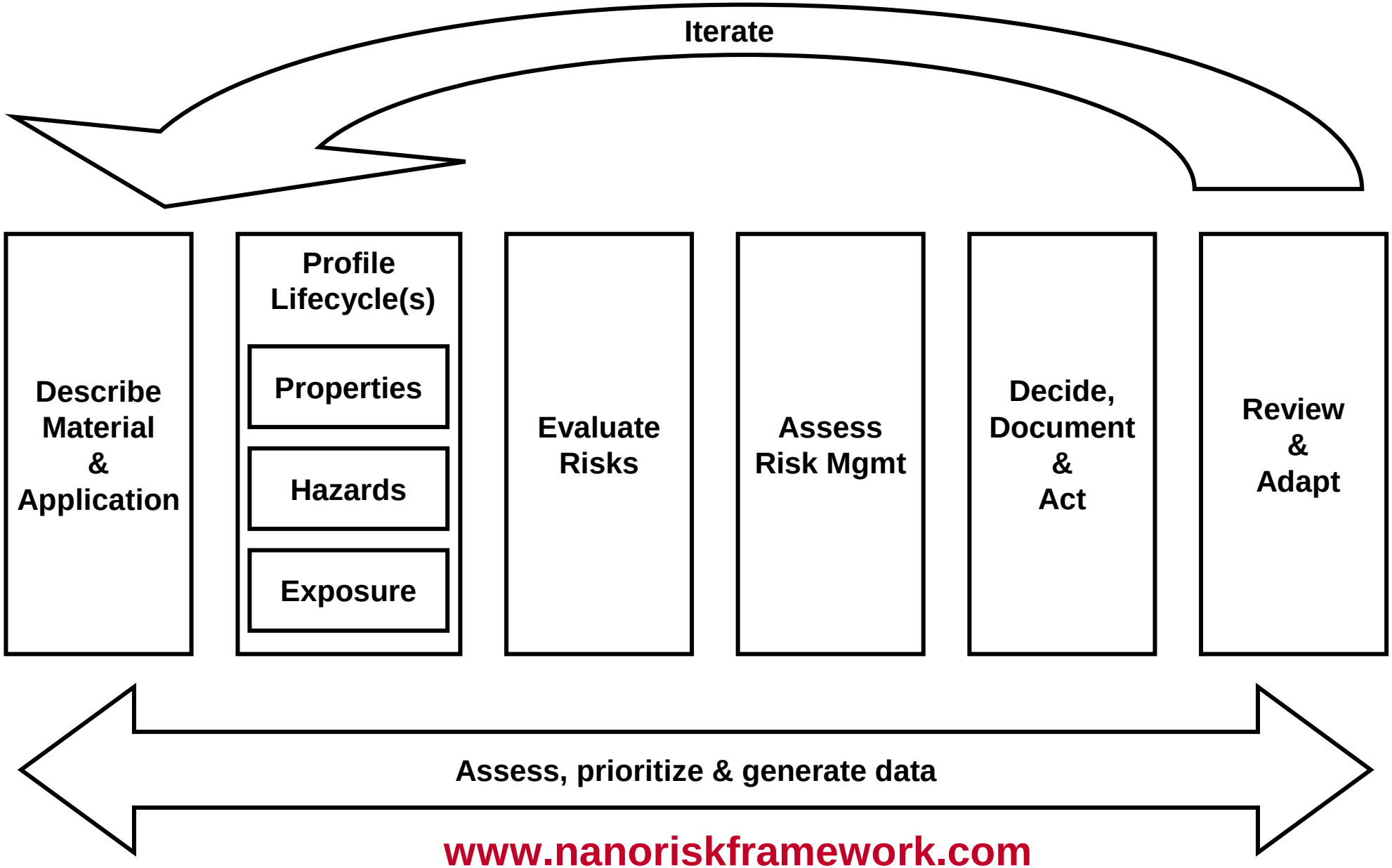
- **Nano TiO2 is not used in toothpaste or as a food colorant*.**
- **Nano TiO2 does not efficiently scatter visible light as individual particles so it will not be used as a “white pigment” to replace pigmentary TiO2 in existing applications.**
- **Nano TiO2 is a niche specialty. It will likely always be a very small fraction of the total titanium dioxide production…. many growth rate projections are greatly exaggerated.**

***(Note: DuPont does not sell pigmentary TiO2 into use in foods either)**

DuPont™ Light Stabilizer 210 (DLS 210)

- **DLS 210 is DuPont Titanium Technologies developmental ultrafine TiO2 product launched in late 2007.**
- **DLS 210 is a surface treated high rutile ultrafine titanium dioxide with a mean size of 135 nm.**
- **Target application is absorbance and scattering of UV light through incorporation into plastics.**
- **The DLS 210 worksheet example and summary have be published globally on website www.nanoriskframework.com in conjunction with the Nano Risk Framework.**
- **Several papers have been published on results of the toxicology studies.**

Environmental Defense – DuPont Nano Risk Framework



www.nanoriskframework.com

Output Worksheet

Organize

Record

Share

OUTPUT WORKSHEET

An editable version of this Output Worksheet is available at www.NanoRiskFramework.com

Nanomaterial Risk Assessment Document — [nanomaterial]

Section 1: Describe Material and Its Applications
Develop basic descriptions — general overviews — of the nanoscale material and its intended uses.

General Overview: [a]

Material Description:
Material source or producer:
Manufacturing process:
Appearance:
Chemical composition:
Physical form/shape:
Concentration:
Size distribution:
Solubility:
State of aggregation or agglomeration:
Material CAS number (if applicable):

Material	CAS Number	Composition

Main applications (current or expected):

Stage of development:

General physical and mechanical properties of this material:

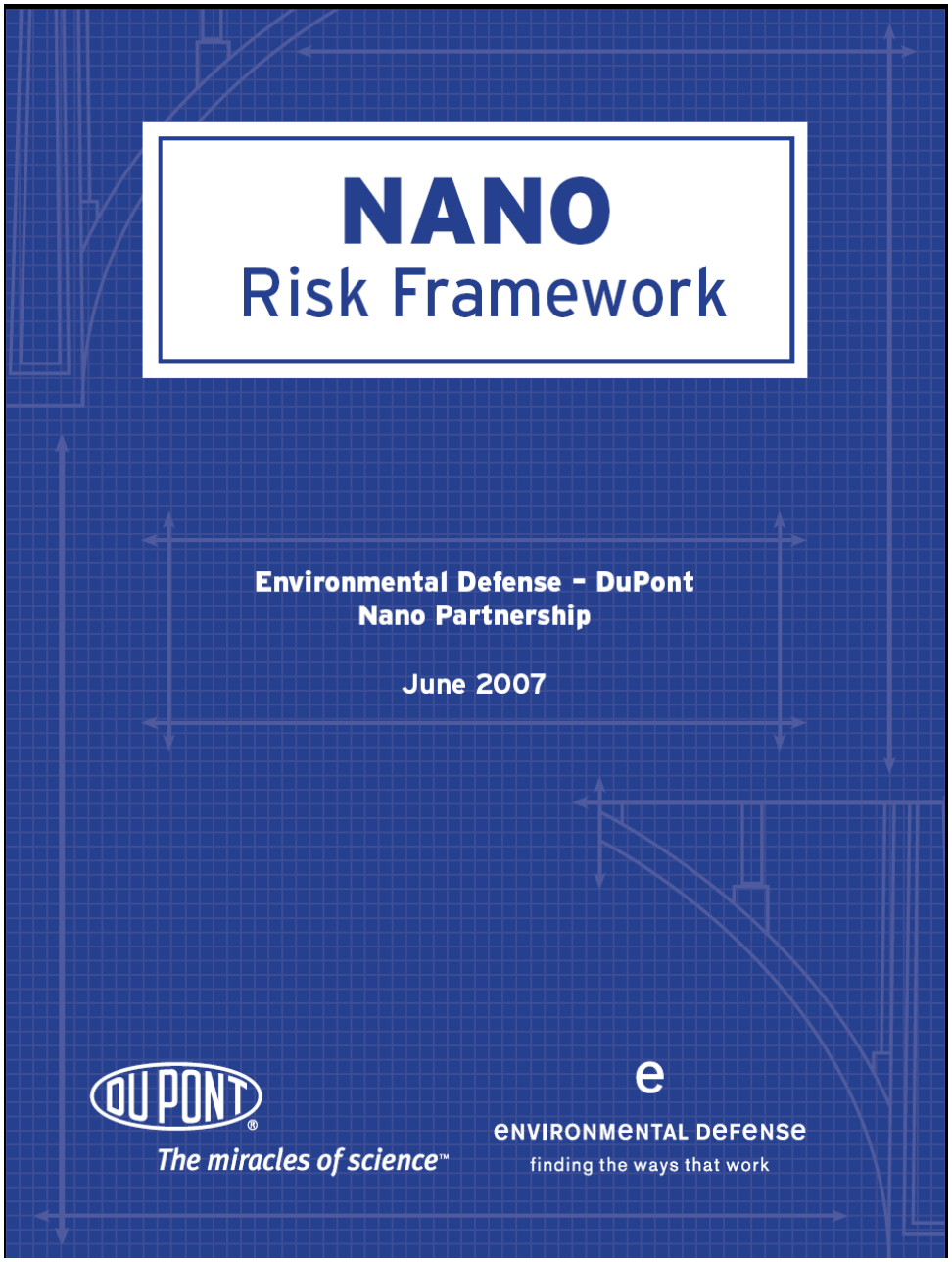
Past experience with this material or a similar material:

Potential benefits/positives of the material:

Potential risks/negatives of the material:
Health:
Environmental:

Sources of additional information:

[a] The general overview should contain descriptions sufficient to guide development of more detailed profiles of the material's properties related to hazard and exposure potential at various lifecycle stages (such as manufacture, use, and end-of-life). This overview should be developed from information in the possession of the user or available in the literature.


NANO
Risk Framework
Environmental Defense - DuPont
Nano Partnership
June 2007
DUPONT
The miracles of science™
e
ENVIRONMENTAL DEFENSE
finding the ways that work

Nano Risk Framework

Objective: To develop and deliver a systematic and disciplined process for identifying, managing, and reducing potential environmental safety and health risks of engineered nanomaterials across all stages of a product's lifecycle.

Scope: Offers guidance on the key questions an organization should consider in developing applications of nanomaterials, and on the information needed to make sound risk evaluations and risk-management decisions.

Audience: Primary audiences are organizations such as companies and public and private research institutions that are actively working with nanomaterials and developing associated products and other applications. Framework can also be usefu to other stakeholders, such as government officials, academia, financial institutions, and nongovernmental public-interest organizations.

Goal: Comprehensive, flexible, practical

A Mix of Familiar and New Elements

- Familiar risk management paradigm
- Development of informational profiles (base sets)
- Information driven
- Reasonable worse case assumptions
- Appropriate bridging
- Applying life cycle thinking

Comprehensive, Flexible and Practical

Comprehensive

Lifecycle approach

Base-sets (Properties, Hazards, Exposure)

Cross-Functional Review

Review and Adapt

Flexible

Appropriate to Stage of Development

Data Generation

Conservative Assumptions

Appropriate Bridging

Expert Judgment

Practical

Familiar risk assessment paradigm

Typical development process

Complements product stewardship